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The Electronic Properties of Graphene Adsorbed on the (111) HfO_2 surface – A First Principles Study

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Abstract

Using density functional theory calculations, we have investigated the electronic properties of graphene monolayer adsorbed on the HfO_2 substrate. Our main research interest here is to explore the reason why the HfO_2 substrate can significantly degrade the transport properties of the adsorbed graphene layer as revealed in the recent experiments. Our calculated results show that graphene monolayer is bounded to the HfO_2 surface via the van der Waals interaction with a binding energy of around 25~40% larger than that on a SiO_2 substrate. The band gap opening at the Dirac point was found to be comparable to that on a silanol SiO_2 surface, but the induced charge accumulation at the graphene/HfO_2 interface is at least one order of magnitude larger than that between graphene and the silanol SiO_2 surface. Moreover, when graphene monolayer was placed on top of the substrate containing an O vacancy, the adsorbed graphene layer becomes n-type doped primarily due to the charge transfer from the O vacancy site in the HfO_2 substrate. Our results further show that the strong interaction between surface O vacancy and the graphene layer not only can result in a relatively larger band gap opening at the Dirac point but also can degrade the linear band dispersion in the band structure of monolayer graphene.

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Keywords: graphene; HfO_2; first-principles calculations

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1. Introduction

Graphene, a monolayer of graphite, has attracted a great deal of attention for its many promising applications in the fabrication of novel electronic devices such as the atomically thin field effect transistors (FET), chemical sensors,photodetectors, and other carbon-based opto-electronic devices. Graphene is a peculiar material with zero band gap and extremely high carrier mobility of a few hundred thousand $cm^2V^{-1}s^{-1}$ primarily due to their two linear dispersion bands crossing at the Fermi level [1-2]. Recently, integration of high-*k* gate dielectrics with the graphene layer has been intensively investigated. Among all the high-*k* dielectric materials, HfO_2 has been considered as the most potential replacement of SiO_2 in the CMOS transistors because of its good thermal stability in contact with Si, relatively large band gaps, and sufficient conduction band offsets with respect to Si [3]. However, recent experiments showed that the charge carrier mobility in graphene can be significantly reduced due to its interaction with the underlying HfO_2 substrate, resulting in a value lower than that for graphene on the SiO_2 substrate or other substrates like boron nitride [4]. To date, many experimental studies have been undertaken to reveal the interactions between graphene monolayer and the HfO_2 substrate, but only a few theoretical investigations have been conducted to realize the geometry, binding energies, and the electronic properties of graphene monolayer adsorbed on the HfO_2 substrate. Recently, Kamiya *et al*. reported their first-principles study on the properties of graphene monolayer adsorbed on a perfect HfO_2 substrate [5]. Nevertheless, the influence of oxygen vacancy in HfO_2 on the electronic properties of graphene monolayer remains unclear, and many important issues, such as the origins of the carrier mobility degradation, are still open to question.

2. Methodology

In this work, we used the well-established Vienna *ab initio* simulation package (VASP) to perform all the calculations [6-8]. The atomic structures, energetics, and electronic properties were calculated based on density functional theory (DFT), while the exchange-correlation interactions among the electrons were treated by the local density approximation (LDA) [9]. The valence electron wave functions were expanded in plane-wave basis sets with a cut-off energy of 500 eV, and the projector augmented wave (PAW) method was used to describe the core-electron interactions. The Brillouin zone samplings were performed with a 6×6×1 k-point grid for geometry optimization, and using an increased 9×9×1 k-point grid for the self-consistent calculations of the energetics and the electronic band dispersion. During the geometry optimizations, all atoms in the supercell were relaxed using the conjugated gradient method until the residual force acting on each constituent atom becomes less than 0.05 eV/Å.

To begin with the calculations, we first constructed the HfO_2 slab model using an oxygen-terminated cleaved (111) surface of *c*-HfO_2, which contained five HfO_2 layers with the lattice constants of $a = b = 3.518$ Å, $c = 12.927$ Å, and $\alpha = \beta = 90°$, $\gamma = 120°$. A 3×3 lateral periodicity of graphene monolayer was then placed on a HfO_2 slab with a 2×2 lateral periodicity. The lattice mismatch between graphene and the HfO_2 substrate is ~4%, and a 20Å-vacuum region was also inserted along the *z*-direction above the graphene layer. Furthermore, to investigate the effect of oxygen vacancies on the graphene layer, we considered three different oxygen vacancy sites in the HfO_2 substrate, which are located in the bulk (1), near the surface (2), and on the top surface regions, respectively. Fig. 1(a) showed the fully optimized hybrid structure and the positions of oxygen vacancy sites. The coordination numbers (CN) of Hf atoms in the slab model were 7 for the topmost layer, and 8 for the inner layers, which is identical to the Hf atoms in a perfect *c*-HfO_2 lattice. Accordingly, creating an oxygen vacancy in the HfO_2 substrate may result in coordination number change of the Hf atoms: for site (1), the CN of the surrounding Hf atoms changes from 8 to 7; for site (2), the CN of three Hf atoms changes from 8 to 7 and that of one Hf atom changes from 7 to 6; for site (3), the CN of the surrounding Hf atoms changes from 7 to 6. Due to the high symmetry of graphene hexagonal lattice, we considered three representative configurations, H, T, and B, to investigate the interactions between graphene and the topmost oxygen atoms on the substrate as shown in Figure 1(b). Owing to the periodicity, H and B configurations have the same structure for all substrates except for the case that has an oxygen vacancy at site (3).

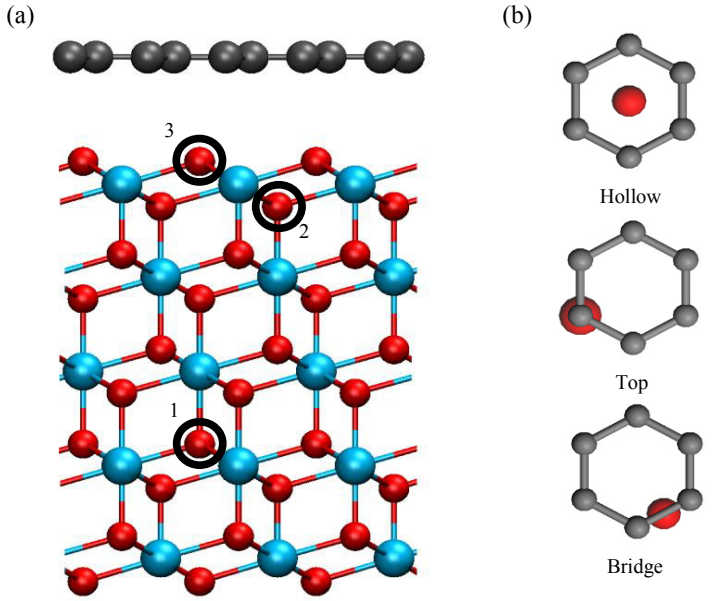

Fig. 1. (a) Side view of the optimized graphene-HfO_2 hybrid structure along with three possible oxygen vacancy sites; (b) Three configurations of graphene monolayer on top of the HfO_2 surface, in which the red atom represents the topmost oxygen atom on the HfO_2 substrate.

3. Results and discussions

3.1. Graphene on a perfect HfO_2 substrate

The interaction between graphene and the HfO_2 substrate was evaluated by calculating their binding energy. Our results show that graphene monolayer is bound to the perfect HfO_2 substrate via the van der Waals interaction with an optimal distance of 3.03 Å for all configurations considered. The most stable structure was found to be the T configuration with a binding energy of 8.96 meV/Å^2, which is about 25% higher than the binding energy between graphene and the SiO_2 siloxane surface (7.11 meV/Å^2) [10]. Thus, the binding energy between graphene and the perfect HfO_2 substrate is around 48% of the van der Waals interaction in graphite (~18.7 meV/Å^2) [11].

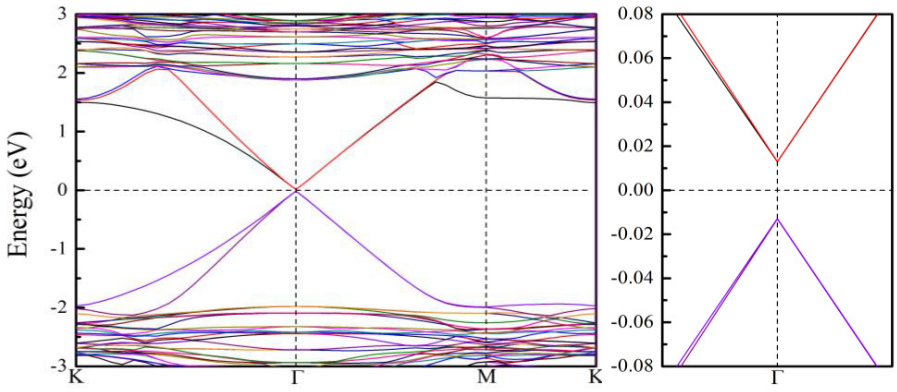

Fig. 2. The electronic band structure of graphene monolayer on a perfect HfO_2 substrate. The inset in the right represents the enlargement of the bands around Dirac point at the Γ point.

Next we analyzed the electronic properties of graphene monolayer placed on top of a perfect HfO_2 substrate. Fig. 2 present the electronic band structure of graphene monolayer deposited on the (111) surface of *c*-HfO_2 substrate. Our results showed that the graphene-HfO_2 hybrid system still retained the major characteristics of the linear band dispersion of a free standing graphene layer but a significant band gap opening of 25.9 meV at the Dirac point was induced due to the disturbance from the interaction with the underlying substrate. Because the induced band gap is higher than k_BT at room temperature, the transport property of graphene can thus be degraded due to its interactions with the HfO_2 substrate. To further investigate the effects of the interaction between graphene and the HfO_2 substrate on the electronic properties of monolayer graphene, we analyzed the change of charge density caused by the adsorption of graphene monolayer onto the HfO_2 substrate. Our results showed that there was no charge transfer between graphene and the perfect HfO_2 substrate, but the valence charge redistribution was observed in the interfacial region and on the graphene layer. The charge accumulation and depletion of the graphene layer was calculated by integrating the charge density difference around the C atoms within their van der Waal radii, 1.7 Å. The values of the charge gain and loss averaged over all C atoms were found to be 0.0038 e/C atom and -0.0056 e/C atom, respectively, leading to a sum of -0.0018 e/ C atom. This result indicates the amount of charge redistribution from the π electrons of graphene to the interfacial region is much larger than that between graphene and the SiO_2 substrate [7], suggesting that the carrier mobility in graphene may be significantly decreased due to its interaction with the underlying HfO_2 substrate.

3.2. Graphene on a HfO_2 substrate with an oxygen vacancy

In the cases of HfO_2 substrate with an oxygen vacancy, we first examined the vacancy formation energies of the three representative vacancy sites. The formation energy of a charge neutral oxygen vacancy in HfO_2 was calculated as

$$E_f^{HfO_2}(V_O) = [E_t^{HfO_2}(V_O) + \mu_O] - E_t(HfO_2) \quad (1)$$

in which $E_t^{HfO_2}(V_O)$ and $E_t(HfO_2)$ are the total energies of the substrate with and without an oxygen vacancy, respectively, and the oxygen chemical potential μ_O is considered as half of the energy of an isolated oxygen molecule. We found that the vacancy formation energies at site (1), (2), and (3) are 6.61eV, 4.97 eV, and 4.93 eV, respectively, indicating that the O vacancy tends to stay near the surface of HfO_2 substrate, which is consistent with the general sense that defects usually move toward grain boundaries or the free surfaces. For all the three cases considered, the most stable structure was found to be the T configuration. The optimal distance between graphene and the HfO_2 substrate and the binding energies are listed in Table 1. The binding energies of these three cases are all higher than that for graphene on a perfect HfO_2 substrate, indicating a much stronger interaction between graphene and the substrate.

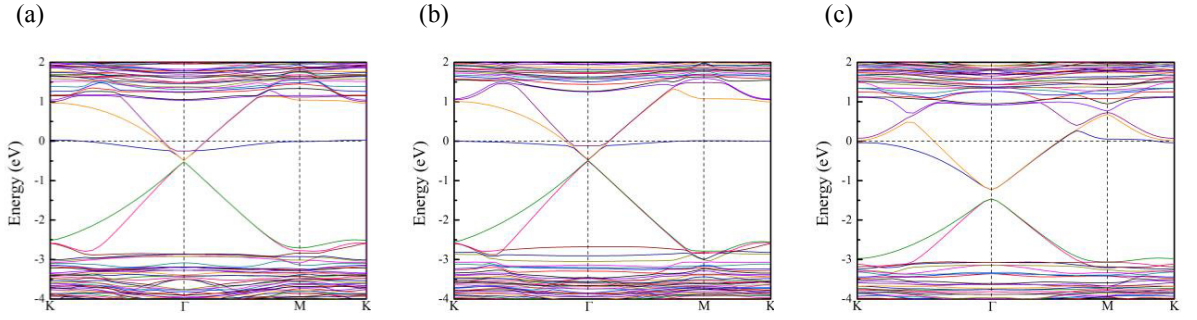

Fig. 3. The electronic band structures of graphene monolayer on the HfO_2 substrate with an oxygen vacancy at the (a) inner, (b) near surface, and (c) surface sites.

We next investigated the electronic properties of a graphene layer placed on top of the HfO_2 substrate with an oxygen vacancy. Fig. 3 presents the electronic band structures of graphene monolayer deposited on the HfO_2 substrate with an oxygen vacancy at site (1), (2), (3). As shown in Fig. 3, substantial electron transfers from the HfO_2 substrate to the graphene monolayer were observed in all three cases, leading to a significant n-type doping effect on graphene. The values of doping level were calculated as the energy difference between Fermi level and the Dirac point, which are listed in Table 1 along with the induced band gaps. Fig. 4 presents the charge density difference after the adsorption of graphene monolayer onto the HfO_2 substrates. As shown in Fig. 4, the charge transfer from the HfO_2 substrate to the graphene layer is mainly originated from the oxygen vacancy sites, resulting in positively charged oxygen vacancies inside the HfO_2 substrates. The n-type doping effect has been proposed by Fallahazad *et al.* in 2010 according to their experimental investigation [12]. Our results strongly support their speculation that the charged oxygen vacancies in the HfO_2 substrate can act as the charge scattering centers to degrade the charge carrier mobility in the adsorbed graphene layer.

Other possible origins for the mobility degradation in graphene are the destruction of the linear band dispersion and the induced corrugation of graphene monolayer found in the cases with an oxygen vacancy on the surface as shown in Fig. 3 and Fig. 4. The oxygen deficient defects on the HfO_2 surface may largely distort the graphene layer and induce a great amount of charge redistribution both on the graphene layer and at the interface between graphene and the HfO_2 substrate (see Table 1). These results suggest that oxygen vacancies in the HfO_2 substrate can be the main origins that significantly degrade the charge carrier mobility in the graphene monolayer.

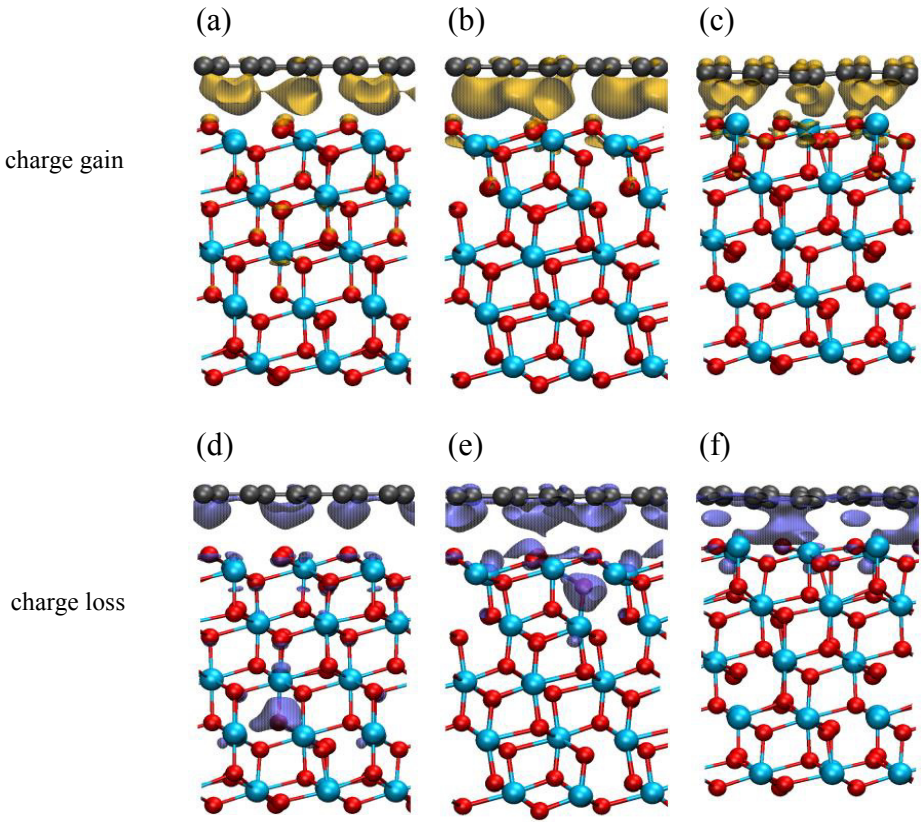

Fig. 4. The charge density difference upon the adsorption of graphene monolayer on the HfO_2 substrate with an O vacancy. (a), (b), (c) present the gain of charge density for the cases with an O vacancy at site (1), (2), (3), respectively; (d), (e), (f) present the loss of charge density for the cases with an O vacancy at site (1), (2), (3), respectively.

Table 1. The optimal distances d_O (Å), binding energies E_b (meV/Å^2), induced band gap E_g (meV), doping level (eV), and charge gain and loss calculated by integrating the charge density difference around the C atoms within their van der Waal radii (e/C atom) for graphene monolayer adsorbed on the HfO_2 substrate with an oxygen vacancy at various sites.

					Charge gain and loss		
Vacancy site	d_o	E_b	E_g	Doping level	Sum	Gain	Loss
1	3.02	9.73	29.61	0.491	0.0016	0.0061	-0.0045
2	3.01	9.55	11.78	0.476	0.0006	0.0059	-0.0053
3	2.44	41.16	234.20	1.227	0.0027	0.0359	-0.0332

4. Conclusion

In summary, we have performed first principles density functional theory calculations to investigate the geometry, binding energies, energetics, and the electronic properties of graphene monolayer adsorbed on the HfO_2 substrate. Our results showed that graphene monolayer is weakly bounded to the HfO_2 surface via the van der Waals interaction with a binding energy of around 25~40% larger than that on the SiO_2 substrate. The band gap opening at the Dirac point was found to be comparable to that of graphene monolayer on a silanol SiO_2 surface, but the induced charge accumulation at the graphene/HfO_2 interface is at least one order of magnitude larger than that between graphene and the silanol SiO_2 surface. Furthermore, when an oxygen vacancy was present in the HfO_2 substrate, the adsorbed graphene layer became n-type doped primarily due to the charge transfer from the oxygen vacancy site in the HfO_2 substrate. Our results further show that the strong interaction between surface oxygen vacancy and graphene monolayer not only can result in a relatively larger band gap opening at the Dirac point but also can degrade the linear band dispersion in the band structure of monolayer graphene. We also found that the presence of surface oxygen vacancy on the HfO_2 substrate can cause the corrugation of the adsorbed graphene layer, which may further degrade the charge carrier mobility in graphene.

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